

# Linear electro optic coefficients $r_{13}$ and $r_{33}$ of in barium-calcium-titanate crystals doped with rhodium ( $\text{Ba}_x\text{Ca}_{1-x}\text{TiO}_3 : \text{Rh}$ ) at 633 nm and 850 nm

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We present the electro optic properties of rhodium-doped barium calcium titanate (BCT) crystals of the congruent melting composition  $\text{Ba}_{0.77}\text{Ca}_{0.23}\text{TiO}_3$ , in carrying out two types of measurements: electro optic (EO) and absorption. The studied coefficients are  $r_{13}$  and  $r_{33}$  as ordinary and extraordinary waves are involved respectively, the polarized absorption spectra of rhodium-doped barium-calcium-titanate (Rh: BCT) are recorded from 400 nm to 1100 nm.

We propose an experimental investigation of the EO coefficients, for two different wavelengths corresponding to strong and weak absorption, based on an interferometric set-up. A static electric field is applied out the sample under study, leading to the measurement of the  $r_{13}$  and  $r_{33}$  coefficients. While the phase transition is shifted to the low temperature in compared with  $\text{BaTiO}_3$  the electro optic coefficients save a high values. Because of the phase transition at low temperatures the values of the coefficients are high compared with  $\text{BaTiO}_3$ .

**Keywords:** Electro-optic, rhodium doped barium titanate-calcium, photorefractive materials,

## I. Introduction

Photorefractive rhodium doped barium titanate (Rh:  $\text{BaTiO}_3$ ) crystal is known to be sensitive in infrared light range [1-2]. They are used in many photorefractive [3] applications such as phase conjugate mirrors and two-beam coupling experiment [4] the high efficiency is due to their large electro optic (EO) coefficients at room temperature [5].

Barium- calcium titanate is a new photorefractive material. A main advantage compared with barium titanate ( $\text{BaTiO}_3$ ), is the disappearance of the phase transition tetragonal-orthorhombic at 9°C, at least down to - 1200°C [6].

Whether rhodium-doped BCT is a real alternative to Rh:  $\text{BaTiO}_3$  depends on the photorefractive properties of this new material [7]. In this contribution a detailed the effet of rhodium doping on the Barium-calcium-titanate  $\text{Ba}_x\text{Ca}_{1-x}\text{TiO}_3$  (BCT) and, in carrying out two types of measurements: electro optic and absorption.

We propose an experimental investigation of the EO coefficients, for two different wavelengths corresponding to strong and weak absorption, based on an interferometric [8] using application of a static electric field and leading to the measurement of the coefficients  $r_{13}$  and  $r_{33}$  separately and compared to undoped BCT and doped rhodium of  $\text{BaTiO}_3$ .

## II. Experimental results

### II.1. Sample

Barium-calcium-titanate crystals of the congruently melting composition  $\text{Ba}_x\text{Ca}_{1-x}\text{TiO}_3$  (BCT) are grown by the Czochralski technique at 1592°C. A more detailed description of the crystal-growth procedure

is given in [6]. Doping is performed by adding  $\text{Rh}_2\text{O}_3$  with 1000 ppm of Rh in the melt. After cooling the crystal is got mono-domain by a thermo-electric treatment. Sample of optical quality are without defect of crystallization. The undoped sample is faint yellow, and the doped sample has a green-blue coloration. The dimensions of the sample are  $5.5 \times 5.53 \times 4.1$  mm<sup>3</sup> respectively along X, Y and Z axis.

### II.2. Absorption measurement

Absorption spectra are measured with a Perkin-Helmer spectrometer, and graphics are shown in figure 1. The absorption coefficient polarized ordinary ( $\alpha_o$ ) and extraordinary ( $\alpha_e$ ) are calculated from the difference of the transmitted light intensity through the sample and a reference light intensity using the refractive indices of BCT [9] to take into account the reflection at the interferences. A broad absorption band is observed in the visible region (figure 1). These coefficients decrease from  $\alpha_o = 5.15 \text{ cm}^{-1}$  (633 nm) to  $\alpha_o = 1.66 \text{ cm}^{-1}$  (850 nm). The results show that the doping of rhodium influences the profile of the BCT absorption specter as well as a strongly marked anisotropy in the visible ( $\Delta\alpha = 1.13 \text{ cm}^{-1}$ ) compared has ( $\Delta\alpha = 0.25 \text{ cm}^{-1}$ ) at 850 nm; the absorption values for ordinarily polarized light are larger in visible especially at 633 nm ( $\alpha_o = 5.15 \text{ cm}^{-1}$ ) than the values obtained with extraordinary light polarization ( $\alpha_e = 4.03 \text{ cm}^{-1}$ ).

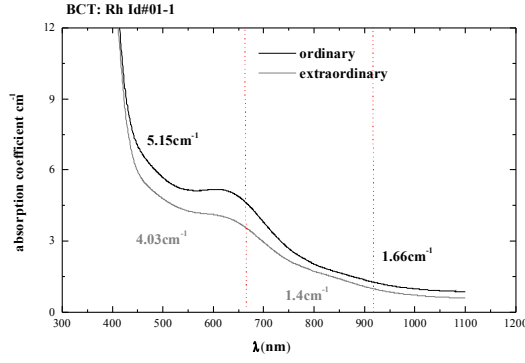


Fig. 1: The absorption coefficient measured for ordinary ( $\alpha_o$ ) and extraordinary ( $\alpha_e$ ) polarization in coherent light from 400 nm to 1100 nm

An absorption study of BCT and BCT doped rhodium has been made by Veenhuis [10] concerning different concentrations of the doping of rhodium. The results show that the absorption graphics of crystals of BCT and these of low concentration of crystals are similar to these of pure BaTiO<sub>3</sub>. A high concentration of rhodium doping (1000 ppm) makes an absorption band appear about 630 nm, which concords with the measurement. So rhodium induces large absorption in the visible on the absorption specter of BaTiO<sub>3</sub> and BCT.

### III. electro-optic measurement

#### III.1. Theory

At room temperature, BCT has the same symmetry as BaTiO<sub>3</sub>. Like BaTiO<sub>3</sub>, the electro-optical tensor  $r$  of BCT is characterized by three independent coefficients and different from zero  $r_{33}$ ,  $r_{13} = r_{23}$  and  $r_{42} = r_{51}$ . By applying an electric field along the  $z$  direction and light propagating in the  $y$  direction with polarization along  $x$  or  $z$  directions, we can easily measure  $r_{13}$  or  $r_{33}$  respectively.

The induced refractive index change along the  $x$  (equivalently  $y$  axis) and  $z$  directions are given by:

$$n_x = n_y = n_0 - \frac{1}{2} n_0^3 r_{13} E_3 \quad (1)$$

$$n_z = n_e - \frac{1}{2} n_e^3 r_{33} E_3 \quad (2)$$

Where  $n_0$  and  $n_e$  are respectively the ordinary and the extraordinary refractive index and  $E_3$  is the applied electric field along the  $z$  direction.

#### III.2. Interferometric measurement

The experimental arrangement is illustrated in figure 2. It consists of a Michelson interferometer with a near infra-red laser diode as light source,

operating at the wavelength  $\lambda = 850$  nm or an He-Ne laser operating at the wavelength  $\lambda = 633$  nm. An EO modulator is placed in one arm of the interferometer and the sample on study is placed in the second arm. EO coefficient is deduced from the compensation of phases. The method is based on the measurement of the reference modulator phase shift to compensate the phase shift induced by a dc field in the crystal under study.

The mirrors of the Michelson interferometer are slightly tilted to observe a linear and parallel fringes pattern. A straight slit parallel to the fringes is adjusted, by the application of a static voltage  $V_m^i$  to the modulator, on a dark or bright fringe. A photo-diode measures the intensity of light behind the slit. An ac voltage is applied on the modulator which changes the optical path at the  $f$  frequency. So the fringes vibrate at the frequency  $f$  and the light behind the slit is modulated at the frequency  $2f$  easily observed on the oscilloscope. The voltage  $V_e$  is applied to the EO crystal under study so that the signal at the frequency  $2f$  disappears, voltage  $V_m^f$  is added to the modulator to compensate the phase-shift induced by  $V_e$  (figure 2 and 3) the signal at the frequency  $2f$  is detected. EO coefficient is then determined by the relation:

$$r_{ijk} = \pm \frac{e_c}{L_c n^3} C_m \left( \frac{V_m^f - V_m^i}{V} \right) + 2 \frac{n-1}{n^3} d_{kij} \quad (3)$$

Where the constant of the modulator  $C_m$  is experimentally determined:

$$C_m = \frac{L_m}{e_m} n_m^3 r_m + 2(n_m - 1) \frac{L_m}{e_m} d_m = 791 \text{ pm/V} \quad (4)$$

With  $e$ ,  $L$ ,  $n$ ,  $V$  and  $d$  are respectively the thickness, the crystal length along the beam direction, the refractive index, the applied voltage and the piezoelectric coefficient, the indices  $c$  and  $m$  referring to the studied crystal and the modulator.

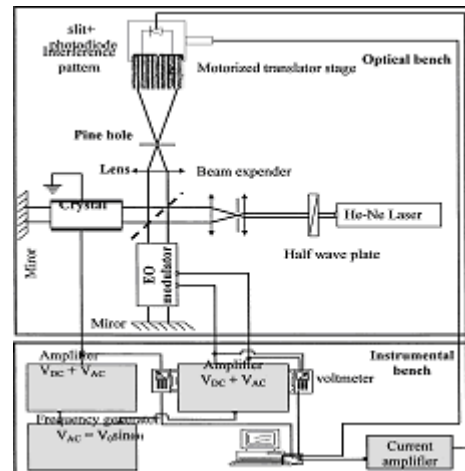


Fig. 2: The Michelson interferometer.

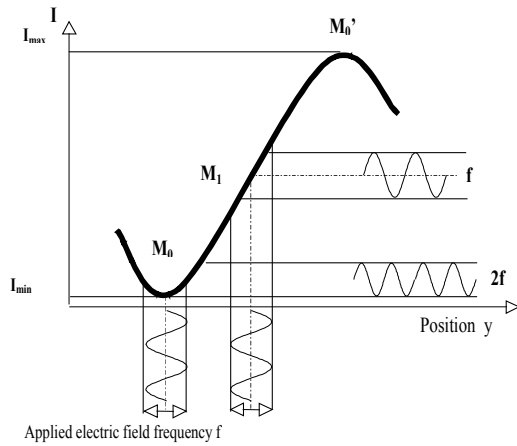


Fig. 3: Transfert function of the interferometer. The light intensity distribution along the y direction perpendicular to the fringes

### III.3. Procedures and results

The method described above used to measure the EO coefficients  $r_{13}$  and  $r_{33}$ . The experimental conditions are summarized in table 1. The coefficients  $r_{33}$  and  $r_{13}$  were obtained when the electric field was applied to the (001) faces, which were sputtered with gold. The coefficient  $r_{13}$  was measured when a light was ordinary polarized along the [100] or the [010] axis, whereas  $r_{33}$  was reached with the extraordinary polarization along the [001] axis. The experimental method is described in detail in ref [8].

Table I: Experimental conditions allowing to measure  $r_{13}$  and  $r_{33}$ 

The experimental procedure described above was reproduced several times to improve the measurement accuracy and to account for drift of the  $2f$  signal quoted above. Figure 4 reports data used to obtain the coefficient  $r_{13}$  and  $r_{33}$  at room temperature.

The plot exhibits the time dependence of the applied dc voltage on the modulator. The difference between the two linear regressions allows us then to determine the voltage  $\Delta V_m$  necessary to counterbalance the effect of the applied electric field on the crystal.

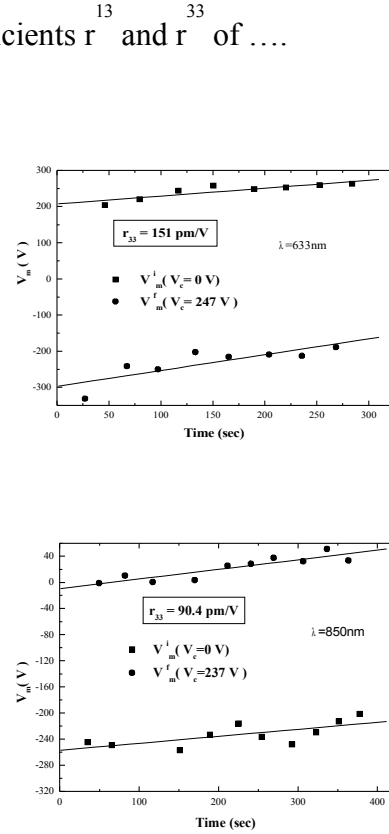


Fig. 4: Example of the plot obtained by measurement of the EO  $r_{33}$  of BCT: Rh at  $\lambda=633$  nm and 850 nm. The circles refer to the voltage applied to the modulator to adjust the optical path length up to a dark fringe. The squares concern the voltage applied to compensate the effect of the applied electric field on the sample studied.  $V_c$  is the voltage applied to the crystal.

Measured coefficient	$r_{13}$	$r_{33}$
Applied electric field	Z	Z
Propagation	X	X
Polarization	X	Z

Electro-optic coefficients (pm / V )	BCT: Rh		BaTiO <sub>3</sub> : Rh		BCT
	(our actual measure)		(our measure) [5]		C. Kuper [6]
	850 nm	633 nm	850 nm	633 nm	514.5 nm
$r_{33}$ (pm / V )	90.4	151	69.8	94	140
$r_{13}$ (pm / V )	68.8	x	12.3	14.9	36

Table II: Linear electro-optic coefficients  $r_{13}$  and  $r_{33}$  of Ba<sub>x</sub>Ca<sub>1-x</sub>TiO<sub>3</sub> doped rhodium at 633 nm and 850 nm compared of BaTiO<sub>3</sub>: Rh [5] and pure BCT [6]

The electro-optic coefficients  $r_{13}$  and  $r_{33}$  are measured for different laser light wavelengths using a Michelson interferometer. Table II compiles our results compared with those reported in the literature of BaTiO<sub>3</sub>: Rh and pure BCT.

The electro optic properties of BCT doped rhodium for two wavelengths 633 nm and 850 nm are very large at room temperature. For  $\lambda = 633$  nm the value  $r_{33} = 151$  pm/V is very large at room temperature compared with the results of BaTiO<sub>3</sub>: Rh [5] but  $r_{13}$  is not determined (bad signal) because the absorption coefficient ordinary polarized is usually high. At  $\lambda = 850$  nm the values measured  $r_{13} = 68.8$  pm/V and  $r_{33} = 90.4$  pm/V for BCT doped rhodium at room temperature are higher by report for the results reported in the literature of BaTiO<sub>3</sub> doped Rhodium [5]. The electro-optical coefficient  $r_{33}$  depend on the wavelength, its value decreases when we goes from the visible at 633 nm to the infra-red at 850 nm

### Conclusion

Electro optic coefficients  $r_{13}$ ,  $r_{33}$  are measured with Interferometric method for two wavelengths 632.8 nm corresponding to the high absorption and 850 nm corresponding to the weak absorption. We may infer that the coefficients EO of BCT doped rhodium are superior compared with those obtained for BaTiO<sub>3</sub>: Rh [5]. Indeed, we showed that the electro optic coefficients  $r_{13}$  and  $r_{33}$  are superior in the case of BCT doped rhodium at 850 nm than in the case of pure BaTiO<sub>3</sub> [11]. The values found near the infrared are largely sufficient to allow interesting and efficient applications in the infrared. It is known that the doping of this crystal with the rhodium increases drastically the photorefractive efficiency near the infrared range.

### References

- [1] M. Kaczmarck, P. Hribek, R.W. Eason, Opt. Communications **136**, 277 (1997)
- [2] N. Huot, J. M .C. Jonathan, G. Roosen, J. Applied Physics. B **65**, 489 (1997)
- [3] N. Huot, J. M. C. Jonathan, G. Roosen, D. Rytz, Optics Communication **135**, 133 (1997)
- [4] N. Huot, J. M. C. Jonathan, G. Roosen, D. Rytz, Optics letters **22**, 976 (1997)
- [5] A. Maillard, S. Bahsine, G. Kugel, D. Rytz and R. S. Klein, Ferroelectrics **296**, 47 (2003)
- [6] Ch. Kuper, R. Pankrath, H. Hesse, Appl. Phys. A **65**, 301 (1997)
- [7] S. Bernhardt, H. Veenhuis, P. Delaye, G. Roosen, Optical. Materials **18**, 13 (2001)
- [8] P. Ney, A. Maillard, M.D. Fontana, J. Opt. Soc. Am. B **17**, 1158 (2000)
- [9] M. Simon, F. Mersch, C. Kuper, S. Mendricks, S. Wevering, J. Imbrock, E. Kratzig, J. Phys. Stat. Sol.(a) **159**, 559 (1997)
- [10] H. Veenhuis, T. Börger, K. Buse, C. Kuper, H. Hesse, E. Krätzig. J. Applied. Physics **88**, 1042 (2000)
- [11] M. Zgonik, Physical. Review B **50**, 5941–5949 (1994).